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Light-Controlled Conductance Switching of Ordered Metal−Molecule−Metal Devices

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ABSTRACT

We demonstrate reversible, light-controlled conductance switching of molecular devices based on photochromic diarylethene molecules. These devices consist of ordered, two-dimensional lattices of gold nanoparticles, in which neighboring particles are bridged by switchable molecules. We independently confirm that reversible isomerization of the diarylethenes employed is at the heart of the room-temperature conductance switching. For this, we take full advantage of the possibility to use optical spectroscopy to follow molecular switching in these samples.

From its very start, molecular electronics has aimed for functional devices. In their groundbreaking paper, Aviram and Ratner presented a molecule acting as a diode, once connected to electrodes.[1] In recent years, the level of device preparation has steadily increased, leading to a major research interest in electron transport in molecular devices[2−22] In parallel, organic chemists have synthesized a truly impressive library of switchable molecules, in which the electronic communication can be controlled.[23,24] These simultaneous developments have stimulated nanoscientists to take up the challenge to create active devices based on molecular switches[7−22] Most of this work has concentrated on four families of molecules. First, Heath and Stoddart created devices incorporating monolayers of rotaxanes or catenanes.[7] In these molecules, an outer ring can move between two positions on a molecular rod or cycle, respectively. Second, several research groups have investigated molecular devices based on redox-active molecules, including viologens, quinones, and Ru-based complexes.[8−13] In general, these experiments are performed in an aqueous environment in order to allow for electrochemical control of the molecule in the junction. A third type of switch is formed by diazobenzenes. These molecules perform a cis−trans isomerization upon illumination, accompanied by a significant change in molecular length and dipole moment.[14−16] Finally, a very promising group of switches is formed by diarylethene molecules, which were pioneered by Irie.[17,24] These molecules can be converted from a conjugated, "on" state (top of Figure 1a) to a cross-conjugated, "off" state (bottom of Figure 1a), upon illumination in the visible region. The reverse process is possible with ultraviolet (UV) light. Diarylethenes have very attractive properties. First and foremost, they are fatigue resistant. Furthermore, their length change upon isomerization is negligible. This allows for minimal mechanical stress when a molecule between two electrodes changes conformation.

Research on switchable molecular devices has taken quite a bumpy road. One reason for this is that independent control experiments have been lacking. Hence, it is difficult to prove that conductance switching is indeed due to the active molecule. A second issue is more fundamental: a molecule may lose its functionality once connected to an electrode.

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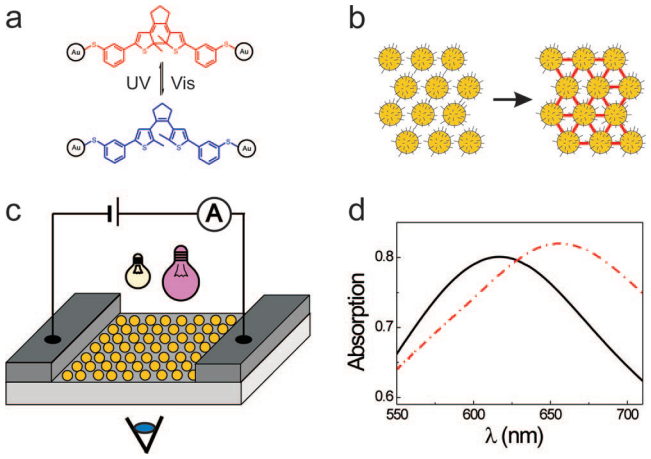

Figure 1. Sample definition and setup. (a) Switchable diarylethene molecules: top, closed, "on" form; bottom, open, "off" state. Switching from on to off is possible by illumination with visible light. The reverse is achieved by UV irradiation. (b) Schematic picture of a two-dimensional nanoparticle network: left, virgin network, consisting of octanethiol-protected gold nanoparticles; right, after the molecular bridging step, the nanoparticles are connected by "on" state diarylethene molecules. (c) Schematic setup to measure light-induced conductance switching (illumination with a Hg lamp). In addition, optical spectroscopy is possible using a low-intensity white-light source. (d) Optical absorption measurements on "sample 1" before (solid, black line) and after (red, dash-dotted line) insertion of "on"-state diarylethene bridges (see (b)). A shift of the surface plasmon peak is clearly observed. This is accompanied by an increase in conductance of a factor of 18.

This is the case for diarylethenes with thiophene end groups, which can only be converted from "on" to "off", once attached to gold.[18,19] Theoretical studies suggest that this is a result of strong electronic coupling between molecule and metal.[25,26] A way to circumvent this is to use nonconjugated spacer groups between the molecule and electrode.[20,21] Unfortunately, this introduces an extra tunnel barrier for electron transport, decreasing the on-state conductance. We designed the dithiolated diarylethenes depicted in Figure 1a, which have a cross-conjugated metaphenyl end group.[27−29] It is with these carefully engineered molecules that we demonstrate reversible switching in gold−molecule−gold devices at room temperature.

For our devices, we utilize two-dimensional nanoparticle arrays, in which diarylethene switches act as molecular bridges between neighboring nanoparticles (see Supporting Information for details).[30−32] In this way, we create an active metamaterial, based on a combination of two nano-objects. The role of the nanoparticles is to define a highly ordered, two-dimensional template.[33] The molecules in turn, form conductive bridges between the particles. Hence, they offer their specific functional properties, or, more exactly, their switchability, to these nanostructured metamaterials. To prepare such samples, we first create hexagonally ordered monolayers of octanemonothiol-covered gold nanoparticles (10 nm diameter), using self-assembly techniques (see Figure 1b). Two gold electrodes are evaporated on each array for conductance measurements (see Figure 1c). Next, we allow dithiolated "on"-state switches to bridge between neighboring gold particles using a thiolate exchange reaction (schematized in Figure 1b). We emphasize that the basic unit in our array is a single metal−molecule−metal device. Indeed, due to the small size of the nanoparticles, each metal−molecule−metal junction incorporates one, or at most a few molecular bridges. The sheet resistance of the network sample represents a spatial average of many independent molecular junctions.[31,32] Consequently, our method forms the two-dimensional, spatial equivalent of sequential single junction experiments as done with break junctions. The latter yield time-averaged conductance values of molecular junctions.[2,34]

To test if molecular insertion is indeed successful, we employ two independent methods (see Figure 1c). First, we measure the conductance G before and after molecular bridging. We find conductance enhancements of over an order of magnitude. This demonstrates that enough molecular bridges have formed to create percolating paths between the gold electrodes. Second, we employ optical absorption spectroscopy in the visible. In Figure 1d, we show optical spectra for a single device (sample 1), both before (black solid line) and after (red dash-dotted line) molecular insertion of on-state diarylethenes. Both curves in Figure 1d show an absorption peak. This feature is due to surface charge oscillations on the nanoparticles, induced by the electromagnetic field of the incoming photons. The physics of this so-called surface plasmon resonance (SPR) is well-described by Mie theory in the dipolar, quasi-static approximation.[35,32] Remarkably, the SPR is extremely sensitive to the direct surroundings of the nanoparticles. Specifically, the permittivity ε of the molecules around the nanoparticles influences the SPR position. This gives us an independent probe to characterize changes in the molecules assembled in the network, due to either molecular exchange[32] or molecular switching. In Figure 1d we see that the SPR is located around $\lambda = 617$ nm for the alkanethiol network. After insertion of conjugated dithiol switches, it shifts to the red (to $\lambda = 656$ nm), since the permittivity of conjugated molecules, such as the closed diarylethenes, is much higher than that of octanethiols.[32] Hence, these spectroscopic data independently confirm that molecular insertion was successful.

In Figure 2, we demonstrate reversible conductance switching of a diarylethene-bridged network at room temperature. The experiment is carried out as follows. First, a sample containing on-state bridges (sample 2) is electrically connected inside an argon flow-cell with quartz windows. This cell is placed within a microscope where it can be illuminated with a 100 W Hg lamp. Two filters are used: one for visible light (Vis-filter, $590 < \lambda < 650$ nm) and one for UV light (UV-filter, $300 < \lambda < 400$ nm). We start our measurements with the light source completely blocked. In that case, the conductance is constant ($t < 0$ in Figure 2). At $t = 0$, we commence illumination with visible light. The conductance decreases rapidly. We relate this to the diarylethene bridges in the network changing from on to off. At $t = 245$ s, we apply the UV filter. Immediately, a steep conductance increase is observed, fully consistent with molecular off to on conversion. After 125 s of UV illumination, we turn to visible light again, repeating the experiment. In Figure 2, we demonstrate eight conductance switching

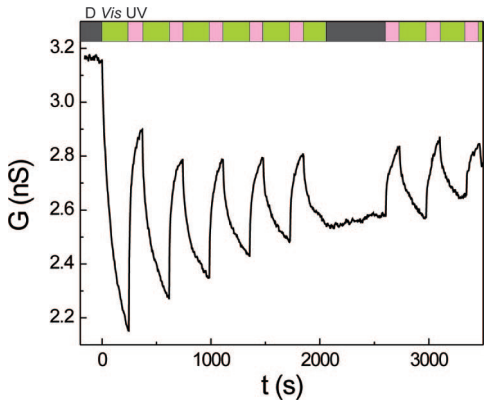

Figure 2. Repeated conductance switching. The conductance G is plotted vs illumination time t, for sample 2 which originally contained on-state bridges only (see Figure 1b). In the dark, the sample conductance is constant ($t < 0$). At $t = 0$, illumination with visible light is commenced (Vis in colored top bar), leading to an immediate conductance decrease. Upon UV irradiation (e.g., at $t = 245$ s, UV in top bar), G increases again. We alternate visible illumination (245 s) and UV irradiation (125 s) eight times, as indicated by the colored bar. For $2095 < t < 2650$ s the sample is left in the dark. The experiment was done in an argon flow cell at room temperature. To determine G, we recorded current−voltage ($I-V$) curves, with $-10 < V < 10$ V, so that for each molecular junction the bias was at most ~10 mV (linear regime). Note that in real time, this experiment lasted over 5 h. (See Supporting Information.)

events. To test if the effect is truly light-related, we kept the sample in the dark after 5.5 periods ($2095 < t < 2605$ s). After this, another three cycles of light-induced conductance switching are performed. Hence, we have created a light-sensitive device, based on carefully optimized switchable molecules,[17,27,28] each coupled to two metal electrodes.

To analyze Figure 2 further, we relate the sample conductance to the percentage of on-state molecules via a percolation model (see Supporting Information).[36] We find that ≈20% of the on-state molecules are converted with each period of visible illumination, whereas ≈70% of the resulting off-state molecules are backconverted by UV illumination. This is a result of our choice to limit irradiation times to avoid photodegradation. In fact, these percentages partially explain the decay in "switching amplitude" in Figure 2. Since fewer than 100% of the molecules are isomerized in each illumination step, it follows mathematically that the switching amplitude decreases with every cycle. Finally two "photostationary states" are obtained: one representing the fractions of on and off molecules after visible-light illumination; the other after UV irradiation (see Supporting Information). Nevertheless, also irreversible processes take place. Excessive UV illumination of the closed form gives irreversible photodecomposition,[24] yielding a further decay of the switching amplitude and device failure. The latter was indeed the final fate for the sample in Figure 2. Experiments in ultrahigh vacuum or, alternatively, on sealed-off samples are expected to yield many more switching cycles.

It is instructive to compare the response times of our devices to those for free molecules in solution, illuminated similarly. In the latter case, we find that ring opening (on to off switching) takes 2 min, whereas ring closure (off to on) takes about 20 s at 293 K. These relatively large time constants are due to the low illumination intensities chosen. More intense light sources (e.g., lasers) should be employed for faster switching. Our percolation model can be used to determine the time constants in our network devices. We find 12 min for ring opening and 1.4 min for ring closure, respectively. This result is consistent with previous pump−probe experiments, where we found that the quantum yield for ring closure decreases from 40% to 7% after metaphenyl switches are connected to gold nanoparticles in solution.[28] The observed increase of the response times upon connecting a molecular switch to gold can have several grounds. First, strong electronic coupling can lead to charge transfer (electron and/or hole) from the excited molecule to the metal. It is for this reason that previous-generation molecular devices switched in one direction only.[18,19,25,26] The metaphenyl switches used here are more decoupled from the gold, suppressing this problem. Energy transfer due to interaction with the mirror dipoles in the electrodes can also lead to a decrease in quantum yield. Finally, it is well possible that some molecules within the networks are sterically hindered in their switching process. Scanning tunneling microscopy experiments on switches in self-assembled monolayers give an indication for this.[29] Further work is required to detail which effect is the dominant influence on the quantum yield reduction observed.

Although conductance switching is clearly observed in Figure 2, it is nevertheless essential to confirm that this effect is due to molecular isomerization indeed. For this, we note first that the monothiol variety of these diarylethenes have recently been demonstrated to switch reversibly after connection to only one gold electrode.[22,28,29] Within the present study, we performed reference experiments on nanoparticle networks with only octanemonothiols, as well as with OPV−dithiol bridges (oligo(3)-phenylenevinylene). These samples showed no switching behavior, although photodegradation was observed (see Supporting Information). Nevertheless, we choose to go one crucial step further and demonstrate a direct connection between molecular conversion and conductance switching in our samples. For this, we apply optical absorption spectroscopy, using the setup schematically displayed in Figure 1c.

Figure 3 connects conductance data to absorption spectra for sample 1. The inset of Figure 3a, shows a spectrum taken before illumination ($t < 0$, black solid curve), featuring an SPR around $\lambda = 656$ nm. At $t = 0$, we start irradiation with visible light. The conductance drops immediately (Figure 3a). At $t = 172$ s, we block the light source. After a period in the dark in which G remains constant, we determine a spectrum. The inset of Figure 3a shows that the SPR has shifted to the blue (blue dash-dotted curve). We relate this to molecular isomerization. Upon on to off conversion, the electrons within the diarylethenes become more localized. Hence, a decrease in ε is anticipated, yielding a blue shift of the SPR. At $t = 452$ s, UV illumination commences and G increases again. We limit UV irradation to avoid degradation effects, which is a reason why G does not return fully. After a further "dark" period, another spectrum is measured.

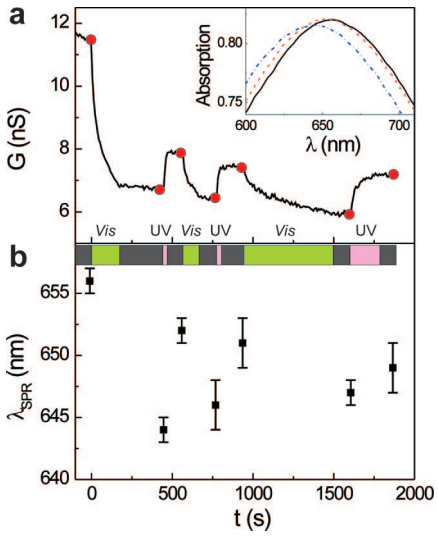

Figure 3. Independent confirmation of molecular switching by optical absorption spectroscopy. (a) Conductance switching of sample 1: at $t < 0$, the sample is in the dark. At $t = 0$, we start illuminating it with visible light, followed by a period in the dark, UV illumination, darkness, and visible light, etc. (see colored bar). Upon visible light illumination, a dramatic decrease in G is observed, whereas G increases upon UV irradiation. At the end of each dark period, an optical spectrum is taken. The conductance at that time t is highlighted by a red dot. (Inset) First three optical spectra (see Figure 1d): black, solid line, spectrum at $t = 0$; blue, dash-dotted line, after first visible illumination, the surface plasmon peak has shifted to lower wavelengths; red, dashed line, after first UV illuminaton, the peak has shifted back to higher λ. Since the off-state switch has a lower permittivity ε than the on isomer, the optical data confirm molecular switching. (b) Plasmon peak position vs illumination time for the entire experiment (note: same time scale as in (a)). All spectra are taken after a period without illumination. The plasmon peak position and the conductance (cf. red dots in (a)) change in unison, connecting conductance switching and molecular switching. The experiment was done in an argon flow cell at room temperature.

Indeed, the SPR has shifted back to higher wavelengths (red dashed curve). From this we conclude that diarylethene molecules are reversibly converted between on and off while bound to the nanoparticle surface. To fully connect both kinds of data, we plot the evolution of the SPR position in Figure 3b for three switching cycles. The SPR position and the conductance show very similar behavior. They toggle in unison from a higher G, higher ε state, to a lower G, lower ε state. Both data sets exhibit a decrease in switching amplitude, as discussed above. We emphasize that our data cannot be explained by heating effects or photocurrents, or by modifications in the nanoparticle networks. Indeed, after illumination, the arrays show no distortion (see Supporting Information). We conclude that reversible shifting of the SPR can only be related to molecular switching within the network. Thus, we have *independently* confirmed that molecular isomerization is the origin of conductance switching.

In summary, we demonstrate selective light-induced conductance switching in ordered metal−molecule−metal networks. To confirm that this effect is truly molecular, we present independent, optical control experiments that reveal a one-to-one relation between molecular isomerization and conductance switching. In addition, it is shown that many switching cycles are possible in these composite structures at room temperature. We note that the open network structure allows for the insertion of a great variety of active molecules. Hence, nanostructured metamaterials with specifically designed properties, based on the functional molecules used, are envisioned.

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Supporting Information Available: Details on sample preparation and experimental techniques, optical spectra of diarylethene molecules in solution, experiments in ambient conditions, photodegradation due to long UV illumination in Ar flow cell, illumination of octanemonothiol-covered nanoparticle networks, illumination of nanoparticle networks bridged by OPV-dithiol molecules, scanning electron microscopy image of sample 1, and discussion of percolation theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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